

GEORGIA INSTITUTE OF TECHNOLOGY  
Engineering Experiment Station  
Atlanta, Georgia

ANNUAL TECHNICAL STATUS REPORT

PROJECT A-781

MASS SPECTROMETRIC STUDY OF LOW FIELD MOBILITY,  
DIFFUSION, AND REACTIONS OF IONS IN GASES

By

D. W. MARTIN  
G. E. KELLER  
D. L. ALBRITTON  
T. M. MILLER  
E. W. McDANIEL

RESEARCH CONTRACT NO. AF 49(638)-1392

1 APRIL 1964 to 31 MARCH 1965  
Issued June, 1965

Performed for  
AIR FORCE OFFICE OF SCIENTIFIC RESEARCH  
OFFICE OF AEROSPACE RESEARCH  
WASHINGTON 25, D. C.

## TABLE OF CONTENTS

	Page
I. INTRODUCTION . . . . .	1
II. OBJECTIVES AND SCOPE OF THE RESEARCH . . . . .	1
III. EXPERIMENTAL APPARATUS AND METHOD. . . . .	3
IV. PROGRESS AND RESULTS OBTAINED. . . . .	6
Phase 1: Studies with the Old Apparatus . . . . .	6
Phase 2: Construction of the New Ultra High Vacuum Apparatus. .	11
V. TRAVEL AND PUBLICATIONS DURING THE REPORT PERIOD . . . . .	20
VI. REFERENCES CITED . . . . .	21

## LIST OF FIGURES

1. View of the Main Vacuum Chamber of the New Apparatus, Complete with Support Structure, Bake Mantles, Main Pump, and Control Circuitry. . . . .	18
---	----

## I. INTRODUCTION

The research that has been performed under Research Contract No. AF 49 (638)-1392 is a segment of a program that has been in progress at the Georgia Institute of Technology for several years. This work has been partially supported from its inception by the Air Force under earlier contracts and grants. Earlier phases of the program have been exhaustively reported in a Technical Report<sup>1</sup> and in the Interim Final Report<sup>2</sup> prepared at the close of the period immediately preceding the present one.

## II. OBJECTIVES AND SCOPE OF THE RESEARCH

The continuing broad objective of this research program has been the development and exploitation of a method of performing mass-spectrometric analyses of ion populations which have drifted for appreciable and controllable distances and times through a gas under low field conditions. Such a method permits direct positive identification of the ion species that are present under given conditions, such as those of a mobility measurement. It is further possible to make separate measurements of the mobilities and in principle also the diffusion coefficients of each species present in systems where more than one type of ion may occur. Finally, by means of controlled variations of the drift conditions, it is possible to observe and study any ion-molecule reactions that may be occurring in the gas.

Definite identification of the ion species under observation has long remained one of the most vexing problems in many areas of gaseous electronics, most notably in situations such as mobility measurement where the ions remain in the gas for appreciable times and suffer many low energy collisions. Even if the initial ion production pattern of the source in use is well understood

from conventional mass spectrometer studies, the ion population may subsequently be altered radically by ion-molecule reactions of any of several general types. These include (1) transfer of the ionic charge to another species of molecule of lower ionization potential, often an impurity, and (2) the formation by essentially chemical reactions of secondary ions, often of molecular types that do not even exist as neutral molecules. Another possibility that has often been discussed<sup>3</sup> is (3) the formation of more or less stable "clusters" by the polarization attachment of one or more neutral molecules to the ion. The reaction cross sections for any of these processes may be very large, so that they may be of importance even if one of the reactants is an impurity of very low relative concentration.

Much of the existing information about ion-molecule reactions has been obtained with "high pressure" mass spectrometers, in which the gas pressure in the source region may be made great enough that some of the newly formed ions may suffer one or more collisions before passing out of the exit slit into the high vacuum of the spectrometer proper.<sup>4</sup> The mean collision energies are generally well above thermal values, and the number of collisions per ion is small, so that it has not generally been possible to approach the equilibrium low field ion spectrum with such instruments. Several other experiments had been reported<sup>5</sup> several years ago that involved the mass-analysis of an ion population present in a truly high pressure region, but none of these had been designed with quite the same objectives and given quite the same combination of features as the apparatus that has been developed in this program.

Relatively recently, groups at several other laboratories have constructed apparatus that is similar at least in general concept to that evolved in the present program, and have undertaken studies having very similar objectives.



Results that have been reported<sup>6-8</sup> have been for the most part in quite good agreement with results which we have obtained, as will be discussed further in Section IV.

### III. EXPERIMENTAL APPARATUS AND METHOD

An apparatus has been developed in this program which we call a "drift-tube mass spectrometer." A large stainless steel, vacuum tight chamber (the drift tube) contains an ion source and an array of annular electrodes with which there can be established a weak axial electric field in the region along the axis of the tube. A series of differentially pumped apertures leads from the center of the end plate of the drift tube into a mass spectrometer. The drift tube is filled with the gas to be studied. Ions are formed locally by the source in a region on the axis of the tube some distance from the end containing the sampling aperture, and the ions are caused to drift toward that end by the axial field. A sample of the ion population present in the region near the end plate is pushed out through the first aperture by the gas streaming from the relatively high pressure drift tube into the pumped region beyond the aperture; a small fraction of these ions which happen to be moving very near the axis find their way through a second aperture and a slit located further along the axis into the high vacuum region of the mass spectrometer, where they are accelerated and analyzed.

The ions are generated in the source by a magnetically collimated ribbon-shaped beam of electrons of relatively well defined and controllable energy, so that the primary ionization region is well defined spatially, and it is possible to generate selectively only those species of ions whose appearance potential is less than the electron acceleration voltage. The electron beam may

be pulsed by means of a control grid, so that ions are produced only in short bursts. The source is movable, so that the net drift distance from the primary ionization region to the sampling region is continuously variable from about 1 cm to more than 30 cm. The gas pressure in the drift tube may be made greater than 1 torr before the gas throughput of the differentially pumped apertures causes a prohibitive loss of vacuum in the mass spectrometer; with nitrogen gas in the old apparatus, pressures up to about 0.7 torr are possible before the pressure in the first pumped region becomes great enough to attenuate seriously the net ion flow into the spectrometer. With this range of drift tube gas pressure and drift distance, the average number of collisions suffered by each ion before it is analyzed is readily made greater than  $10^4$ ; in a pure gas this is quite sufficient to assure that the true equilibrium composition of the ion population is realized.

A noteworthy feature of the apparatus is that the entire differential pumping region is very carefully shielded from all stray electric and magnetic fields, and the apparatus may be operated successfully without any applied electric field in this region to guide or focus the thermal energy ion stream through the series of apertures. Obviously, the fraction of the ions streaming from the first aperture which find their way through all of the others to the analysis region is very small under these field-free conditions. In order to enhance the intensity, a small accelerating potential (typically 1.5 Volts) is normally applied across the region between the first and second apertures. However, the ability to obtain at least limited data under conditions in which the ions are not accelerated at all from thermal energies until they have reached a high vacuum region is very useful in verifying that the thermal energy equilibrium ion population present in the drift tube is not altered by energetic

collisions in the sampling region of the apparatus.

Because it is often necessary to deal with extremely small ion currents in the mass spectrometer, the detector we have used is an electron multiplier, operated with a high-gain pulse amplifier and a scaler as a discrete counter for single ions. The multipliers which have been used can be adjusted to count with an efficiency believed to be about 50% with a spurious background count rate of less than 10 counts per minute. It has been possible to obtain useful data with net count rates of the same order of magnitude, corresponding to ion currents of less than  $10^{-19}$  amperes.

The individual ion pulses from the detector are sorted electronically according to their arrival times relative to the voltage pulse that initiates the ion burst in the ion source. Thus the transit time of each ion through the drift tube and the analyzer is measured, providing a detailed spectrum of the drift times of the ions through the gas. The drift velocity of the ions is readily obtained from the mean drift time, and in principle the diffusion coefficient can be obtained from the spread in drift times. Under favorable conditions, other details of the drift-time spectrum such as the skewness of the distribution can be expected to yield information about the rate coefficients of ion-molecule reactions that either create or destroy the particular species of ion observed. In addition, comparison of the drift-time spectra of two different ion species that are genetically related to each other through an ion-molecule reaction can quite easily yield convincing evidence of the existence of the genetic relationship.

The foregoing discussion has been presented in general terms so that it applies equally, both to an old apparatus that was constructed prior to the present period, and to a new and greatly improved version on which construc-

tion was initiated within this period. The general experimental method and concept of the two instruments are essentially the same. The nature of the major differences and the motivations for them will be discussed in the next section.

#### IV. PROGRESS AND RESULTS OBTAINED

The experimental program that has been conducted during the period covered by this report has consisted of two relatively distinct phases. Briefly, these were (1) the completion of studies that were already underway using the old version of the apparatus, and (2) the construction of a new apparatus making consistent use throughout of the most modern techniques of ultra high vacuum. These two phases have proceeded concurrently during this period, and will be discussed separately.

##### Phase 1: Studies with the Old Apparatus

Studies of the system of nitrogen atomic and molecular ions in nitrogen gas have now been carried as far as it is believed they profitably can be with the old apparatus, and have been brought to a conclusion. The results of this study have been described in detail in a technical report<sup>9</sup> issued previously, so they will be discussed only in rather general terms here.

The general decrease in our best values for the drift velocities of the nitrogen ions from those reported in our 1963 Paris paper,<sup>10</sup> which was mentioned in our last report,<sup>2</sup> has been confirmed by all subsequent evidence. Although the Paris data had quite good internal consistency, they had been obtained over a rather short period of time, and it now is clear that they contained systematic errors. In the period since then, all of the factors which might lead to such errors have been checked exhaustively, and it is firmly believed that the present results<sup>9</sup> are correct.

It was stated in the last report<sup>2</sup> that this change in our values tended to reduce the extent of our agreement with the results of other investigators, specifically those of McAfee and Edelson<sup>6</sup> and those of Dahlquist.<sup>11</sup> On reexamination, this does not clearly appear to be the case. The results of McAfee and Edelson were, like ours, drift velocity measurements on mass-analyzed ions. However, they were for the most part limited to a considerably higher range of  $E/p_0$  than were our results, so that the comparison was indirect and involved some extrapolation. The agreement which we had claimed between their results and ours in 1963 had been based mainly on extrapolated low-field mobility values that had been inferred from the two sets of data. On making direct comparisons with their plots of drift velocity versus  $E/p_0$ , however, it appears to us that their measurements really connect somewhat more reasonably with our present results, for the most part. In particular, several points which they had obtained by a special technique for  $N_4^+$ , at much lower  $E/p_0$  than the rest of their data, are in very good agreement with our present results. The results of Dahlquist<sup>11</sup> did not include mass identification of the ion species involved, and from our detailed results it appears likely that he was dealing with complex mixtures of species in many of his measurements.

More recently, Saporoschenko<sup>8</sup> has constructed an apparatus which permits drift velocity measurements of mass identified ions. He has obtained results for the nitrogen ions in nitrogen which are in remarkably good agreement, for the most part, with our present values for the drift velocities. For completeness it must be added, however, that we disagree significantly with Saporoschenko on a part of the interpretation of the drift velocity data in terms of mobilities. More will be said on this question below.

Despite the general decrease in all of the drift velocity values as com-

pared with the Paris paper data, the present data are in good agreement with the former with regard to the relative magnitudes and the general form of the  $E/p_0$  dependence of the drift velocities of the several ions in nitrogen, i.e.,  $N^+$ ,  $N_2^+$ ,  $N_3^+$ , and  $N_4^+$ . The present data are of higher resolution and show more details of the time spectrum, and of certain variations of these details with  $E/p_0$  and with the gas pressure at constant  $E/p_0$ .

From these results the following general conclusions have been drawn: of the four common ions seen in nitrogen, only the atomic ion  $N^+$  appears unambiguously to be formed only at or near the ion source, to retain its identity throughout its transit through the gas, and hence to have a well defined mobility in the classical sense of the term. We find this mobility to have the constant value of  $2.47 \text{ cm}^2/\text{volt-second}$  for the entire range of all the experimental parameters covered in our data, i.e., for  $E/p_0$  from 7 to 70 volts/cm-torr and for gas pressures from 0.050 to 0.250 torr. Because of this constancy it appears reasonable to assume that this value represents the true "zero field" mobility of this ion. Under all experimental conditions explored, the  $N^+$  ion is the fastest of the four ions, and it thus appears that no "mobility" (real or apparent) larger than 2.47 should be observed in pure nitrogen.

For none of the other three ions does the same simple situation prevail. It appears from our results that Varney's hypothesis of several years ago,<sup>12</sup> that  $N_2^+$  and  $N_4^+$  ions inter-convert into each other in flight, must be essentially correct. At the lowest  $E/p_0$  and the highest pressure values, the population of these two species is found to be predominantly  $N_4^+$ , and from the detailed shapes of the time spectra it appears that most of the ions have spent most of the time of their transit through the gas as the slower  $N_4^+$  ion. Conversely, at the highest  $E/p_0$  and lowest pressure values, the ion population is

predominantly  $N_2^+$ , and it appears that most of the ions have spent most of their transit time as the faster  $N_2^+$  ion. However, under no conditions within the ranges of the parameters covered in these data are "pure" drift spectra obtained for either of these species which are essentially independent of the influence of the other. Apparent mobilities that can be deduced from the mean drift times are, remarkably enough, found to be constant with varying  $E/p_0$  at low  $E/p_0$  for both species, in different suitably chosen pressure ranges. However, it is our conviction that such values do not represent true mobilities in the classic sense, and that they should not be reported as such.

The situation with regard to the  $N_3^+$  ion remains uncertain. A well defined mean drift velocity is found that varies smoothly with  $E/p_0$ , but the apparent mobility deduced from these data is not constant. The genetic relationships with the other ion species, if any, are not at all clear. We remark only that the drift velocity becomes very close to that of  $N^+$  at high  $E/p_0$ , a fact whose significance is unknown.

For a more detailed discussion of these data, of the comparisons with the results of other workers, and of our interpretations, reference is again made to the Technical Report<sup>9</sup> mentioned previously. A lengthy paper presenting these results and containing a quite general discussion of the impact of this type of data on the field of ion mobility measurements has been accepted by The Physical Review.<sup>13</sup>

The hope that detailed analyses of the drift time spectral shapes could be made to yield values for diffusion and reaction rate coefficients continues to be frustrated by the complexity of the ion population and the obvious interrelationships of the several species in nitrogen. Although the present data have much improved resolution in the drift time measurements and are much less

perturbed by the effects of impurities than our earlier results have been, it was quite apparent from the widths of the time spectrum peaks obtained that the data are still not good enough for such a detailed analysis to be very realistic. The new apparatus, whose construction is already well underway (see next section), will be much cleaner in both the geometrical sense and with regard to the presence of impurities in the system; hence it was not judged to be worthwhile to press the matter of detailed analyses of spectral shapes any further than already indicated, with the old apparatus. The study of the nitrogen system with this apparatus has therefore been brought to a close, with the remaining questions left for future studies with the new apparatus.

Studies of the system of hydrogen ions in hydrogen gas were reopened and were pursued for a short time with the old apparatus. Separate drift time spectra and drift velocity values were obtained for  $H^+$  and  $H_3^+$  ions over our usual ranges of values of  $E/p_0$  and pressure, and at first these appeared to be of quality comparable to the nitrogen results. Saporoschenko had also made measurements on this system, and his drift velocity values<sup>8</sup> again appeared to be in excellent agreement with ours, in general. However, certain inconsistencies in the behavior of the  $H_3^+$  spectra with changes in the pressure caused us to look further. It was noticed that the impurity ion of mass 29 (presumed to be  $N_2H^+$ ) was always present, having under most conditions an abundance that was almost comparable to that of  $H_3^+$ . Drift time spectra for this ion yielded values for its drift velocity that were essentially the same as those obtained for  $H_3^+$  under the same conditions. It was apparent that all data being obtained for  $H_3^+$  must probably be seriously perturbed by the presence of this impurity, and that no really meaningful results would be forthcoming until it was eliminated. Since this was clearly a job for the new ultra high vacuum



apparatus, further studies of this system with the old apparatus have also been terminated. Because of the uncertainties present, no publication of the preliminary results obtained for hydrogen is planned.

At the present time, the old apparatus has been shut down, but for the time being it remains intact. It is planned that it will be used further only as a test chamber for components, such as ion sources, during the remainder of the construction of the new apparatus. When it is no longer required for this service, it will probably be dismantled.

#### Phase 2: Construction of the New Ultra High Vacuum Apparatus

Detailed design of all of the main features of the new apparatus has been completed within this period. Portions of the construction have also been completed, and the bulk of the rest of the construction is underway. Care has been employed in the design to avoid, as far as is possible, the major deficiencies which long experience has revealed in the old apparatus. Enumeration of the main considerations includes the following:

(1) Cleanliness and vacuum integrity of the drift space enclosure, to minimize the intrusion of impurity-derived ion species into the system of ions under investigation;

(2) Geometrical simplicity of the drift space, in order that the real physical boundary conditions on the ion swarm may be adequately represented by tractable mathematical idealizations;

(3) Geometrical accuracy in the shapes of the boundaries of the drift space, the locations of the ion source and the exit aperture, and in the geometry of the ion sampling system;

(4) Maximization of the pumping speed in the region just outside the

drift tube exit aperture, in order that scattering of the ions in this region be minimized. The goals here are (a) to make the ion sampling system as unselective among different ion species as possible, (b) to permit the use when desired of a small focusing or guide field (electrostatic) on the ion stream in this region, without fear of changing the ion population due to energetic collisions, and (c) to permit the use of higher drift tube pressures and thus extend the accessible range of the experimental parameters. The purposes of an electrostatic guide field across this region would be twofold: first simply to gain intensity, and second to reduce the transit time of ions across the region so that statistical scatter in the transit time will contribute less scatter to the observed total transit times (drift time in the gas plus transit to the detector).

(5) Further improvements in overall time measurement resolution.

The importance of these several considerations is apparent from the discussion of the work with the old apparatus in both the preceding section and in past reports. Item (5) is largely a matter of external circuitry and will not be discussed in any detail here. The other four items, however, are rather intimately bound up in the physical design and construction of the major hardware.

The new apparatus differs quite substantially from the old in a number of aspects of its basic design, quite apart from the differences in materials and construction techniques. First, the drift tube proper is to be a relatively lightly constructed cylinder that is entirely contained within the larger main vacuum chamber. It will be assembled without gaskets from very closely fitting parts. It will thus, strictly speaking, not be vacuum tight at all, but the parts will fit closely enough that leakage of the contained sample gas into the surrounding vacuum will be small compared to the gas flow through the sampling

aperture. Thus the leakage should materially increase neither the ambient system pressure nor the gas load on the pumps. The gasket-less design has been chosen for two reasons: first, it makes it easy to provide for very accurate relative positioning of the several parts of the tube assembly, since the closely fitting parts will mate directly together. Second, it will make it possible to bake the drift tube itself at much higher temperatures than are feasible for the gasketed outer chamber, should this prove to be necessary, through the use of some sort of internal heaters (most likely radiant).

The region into which will stream the gas flowing from the drift tube exit aperture will, in this design, be the main vacuum chamber itself. The gas can flow unimpeded away from the aperture region in all radial directions, to the outer part of the chamber, from whence it will be pumped off by the main 6-inch pump system. This arrangement will provide the greatest pumping speed at the region near the exit aperture that we have been able to devise.

A second major design change is that the axis of the drift tube is to be oriented vertically, with the ion source assembly mounted on the top end and the ion sampling and analysis system on the bottom end. This orientation greatly simplifies the maintenance of accurate axial symmetry and alignment, especially accurate axial positioning of the ion source, which must be moveable along the entire length of the drift tube axis.

A neck which actually represents an extension of the drift tube volume will extend from the internal chamber through the top cover of the main vacuum chamber to an external housing or boss, where lead-through seals for electrical and gas feed connections into the drift tube will be located. The mechanism for moving the source will be external, located above the boss, with a long flexible metal bellows, extending down through the boss and neck to the ion

source inside the drift tube, providing the moving vacuum seal. With this somewhat unusual arrangement, the drift tube gas space will be on the outside of the bellows, while the external atmosphere will be on the inside. Thus, the part of the electrical leads to the source which must be flexible, in order to allow the source to move, will be in the outside air and can be made of ordinary flexible insulated wire. Only short, rigid leads from a lead-through seal at the bottom end of the bellows to the source will be inside the drift tube. These will not have to be insulated, with the attendant gas contamination problems this would entail.

Almost the entire experimental assembly has been designed to be assembled on the top cover of the main vacuum chamber, on a stand outside the chamber. The drift tube proper and attached ion sampling system will hang below. The main cover and the boss and source movement assembly will project above. After satisfactory internal alignment of this assembly has been obtained, the entire assembly can be lifted with a hoist and lowered into the main chamber. Then certain flexible pumping connections from the second stage of the sampling system to an auxiliary pump system below the chamber can be completed from below. (However, it is provided that the ion source can also be removed from the top of the assembly without removing the main chamber cover, to reduce the labor involved in replacing the ion source filament.)

A third major design difference is in the configuration of the drift field electrodes. In the old apparatus these were annular discs only about 1/16-inch thick in the axial direction, having a radial width comparable to the axial spacing between adjacent discs (2 inches). While these electrodes provided a relatively uniform and well defined field at points near the axis of the tube, the field at appreciable radii was quite non-uniform and not well known. Fur-

thermore, no simple boundary condition on the mathematical model of the ion swarm could very closely approximate the effect of having the outer wall of the drift space defined by these discs and the grounded outer wall of the vacuum chamber beyond. In the new design the electrode rings, of 6.8-inch inside diameter, will be 1.20 inches thick in the axial direction and will be spaced only 0.03 inch apart. Thus, from the inside, the drift space wall will approximate a continuous, smooth metal cylinder, whose potential changes in steps at the boundaries between the rings. An exact calculation of the field inside such a cylindrical assembly (including the effects of the small but finite gaps between the electrodes) has been made,<sup>14</sup> and the results indicate that the field should deviate less than 0.5% from uniformity at points up to half of the inside radius of the cylinder away from the axis.

For dimensional accuracy, these rings will be machined from a length of very thick-wall stainless steel pipe, and they will be quite heavy. The vertical configuration of the axis will permit them to be simply stacked on ground ceramic spacers and aligned with small ceramic pins.

It has been decided that an rf quadrupole mass spectrometer will be used on at least a trial basis as the mass analyzer. Design drawings for a small 4-inch unit claimed to be capable of a resolving power of about 80 have been obtained. Arrangements have been made for construction of both the quadrupole head unit and the necessary circuitry. From the information available, it is expected that this very compact and convenient device will prove adequate to our needs. However, in the event that this should not prove to be the case, the ion extraction system and the lower end of the main chamber have been so designed that it will still be possible to go back to the Nier-type 60° magnetic deflection mass spectrometer of 6-inch radius used on the old apparatus. The

main chamber has been mounted high enough from the floor to leave room for the spectrometer tube and magnet below it.

The only major design feature on which no final decision has been reached as yet is in the choice of the ion detector to be used with the mass spectrometer. Enough room has been provided to permit any of several choices to be made with no difficulty.

Ultra-high-vacuum (UHV) techniques have been used throughout in the new design. Virtually all internal parts will be made of stainless steel, all seams will be welded on the inside and machined smooth, and all interior parts will be polished. All flanged joints will employ heavy flanges, machined flat and polished. Dead-soft aluminum wire 1/16-inch in diameter is being used as the gasket between mating flat flanges, the bolts to be tightened according to a prescribed pattern with a torque wrench to obtain a controlled deformation of the gasket (each gasket will be used only once). Custom-made baking mantles have been procured that lace snugly about the outside of all external parts of the system, to permit uniform baking at carefully controlled temperatures. The mantles obtained are capable of baking the system at temperatures of close to 400° C, although temperatures up to only about 200° C may be used with the present aluminum gaskets before they weld to the flanges and spoil them. Trapped air spaces inside the vacuum system have been carefully avoided by the usual procedures of slotting or drilling all bolts and screws, etc.

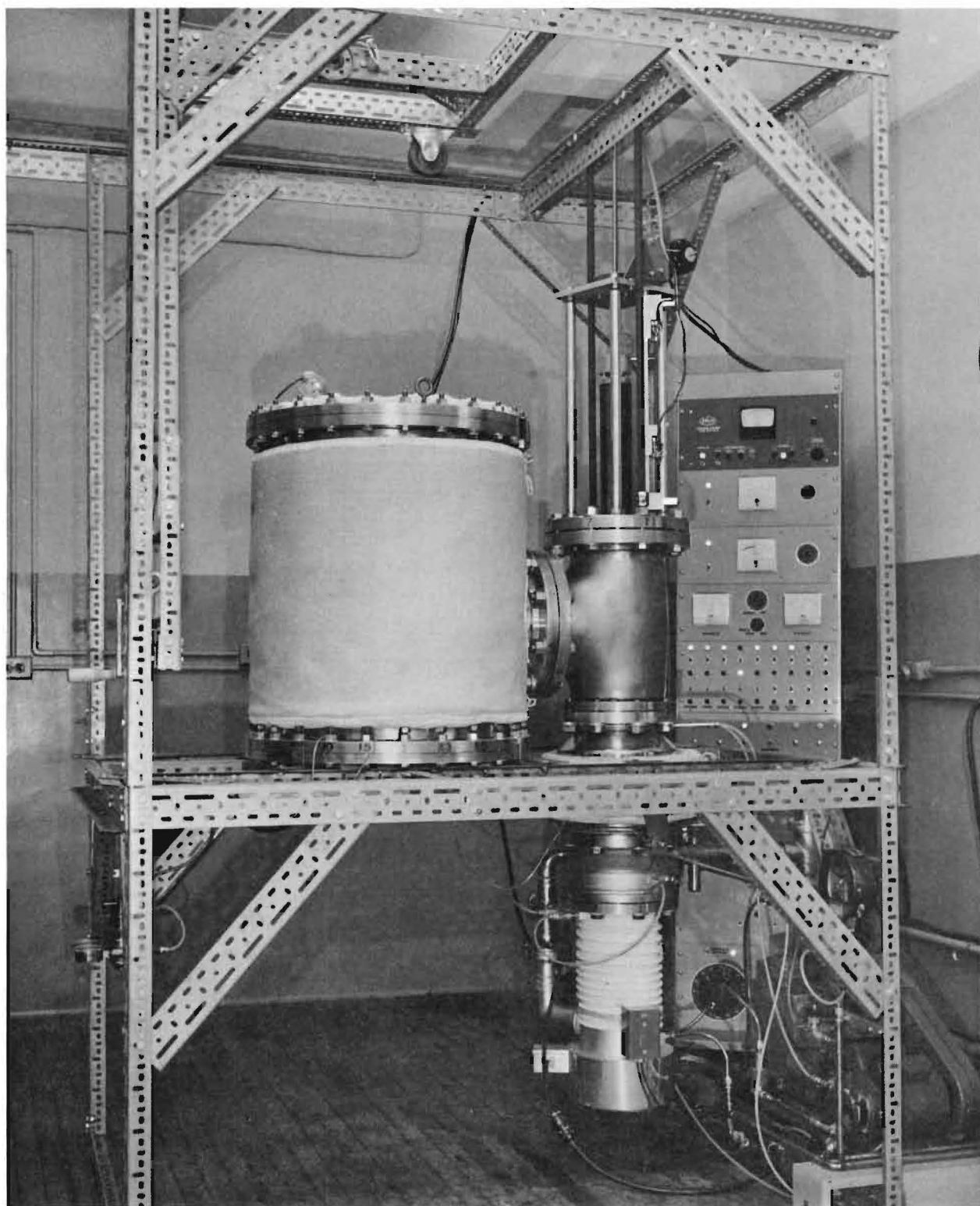
New UHV-design diffusion pumps having flanges designed for metal gaskets have been procured, with water cooled baffles and with sorbent traps instead of cryogenic traps. The main pump on the main chamber will be handling a substantial gas load under normal operating condition, since it must pump away the bulk of the gas which streams from the drift tube exit aperture. It is not

known how rapidly its sorbent trap may tend to "load up" with some of the gases we may wish to study. Hence provisions have been made for the separate bakeout of this trap, as frequently as may be required, without recontamination of the whole system requiring a general bakeout. A homemade isolation valve has been constructed to be located above the trap, between it and the main chamber. This assembly provides UHV isolation from the outside atmosphere, although the internal closure is not strictly vacuum tight at all and is only adequate to the purpose at hand. This expedient proved to be very much less costly than a commercial all-UHV valve of comparable size would have been.

The actual construction, assembly, and testing of the main vacuum chamber, with both its cover plates, the side elbow (containing the isolation valve) for the main pump, and the components of the main pumping system have been completed in the period covered by this report. Also completed was the necessary supporting structure, with the overhead hoist for inserting the experimental assembly into the chamber, the baking mantles for all but the valve elbow, and a carefully engineered control and alarm circuit to provide accurate control of the bakeout cycle and "fail safe" (as far as possible) operation of the vacuum system. A photograph of this entire assembly is shown in Figure 1. This empty system has proved capable of achieving base vacua below  $10^{-9}$  torr, fully two orders of magnitude better than the old system, with the use of only very modest bakeout temperatures.

The detailed design drawings and specifications for essentially all of the other major components have also been completed. Most of the materials are already in hand or are expected to arrive shortly, and arrangements for most of the actual shop work have been completed.

As presently scheduled, all of the major components should be in hand by



1. View of the Main Vacuum Chamber of the New Apparatus, Complete with Support Structure, Bake Mantles, Main Pump, and Control Circuitry.



the early part of the summer. Final assembly of the entire apparatus is expected to be completed by the end of the summer. At least preliminary performance data should be available by the time of the next report on September 30.

## V. TRAVEL AND PUBLICATIONS DURING THE REPORT PERIOD

E. W. McDaniel served as a U. S. delegate at the Symposium on Atomic Collision Processes in Plasma, held at the Culham Laboratories in Abingdon, England, in September, 1964. E. W. McDaniel and G. E. Keller attended the 18th Annual Gaseous Electronics Conference held in Atlantic City, N. J., in October, 1964. (At this meeting, Georgia Tech was chosen to be the site of the 1966 Conference.)

During this period, E. W. McDaniel has presented seminar talks on this research at New York University, Johns Hopkins University, the University of Durham (Durham, England), the University of Virginia, and the University of Maryland. He also delivered an invited paper on the drift tube research at a meeting of the Southeastern Section of the American Physical Society at Chattanooga, Tennessee, November, 1964.

A Technical Report (listed as Reference 9) which generally summarizes the entire development of the old apparatus, and presents in detail the results of the study of nitrogen ions in nitrogen with that apparatus, was issued during the period of this report. A lengthy article presenting the same results, and including a rather general discussion of the significance of this type of data to the low energy atomic collisions field, has been accepted by The Physical Review. (This article is listed as Reference 13.)

Respectfully submitted,

David W. Martin  
Project Director

## VI. REFERENCES CITED

1. Technical Report No. 1, Project No. A-614, Georgia Institute of Technology, Atlanta, Ga. (June 1, 1963). (Available on request.)
2. Interim Final Report, Project No. A-614 (Air Force Grant For Basic Research No. AF-AFOSR 62-306), Georgia Institute of Technology, Atlanta, Georgia (April 30, 1964).
3. E. W. McDaniel, Collision Phenomena in Ionized Gases, Wiley, New York, 1964, pp. 448-451.
4. For a general discussion and extensive references, see E. W. McDaniel, op. cit., p. 452.
5. E. W. McDaniel, loc. cit.
6. K. B. McAfee and D. Edelson, Proceedings Sixth International Conference on Ionization Phenomena in Gases, Societe d'Edition et de Recherche Publicitaire Imprimeurs, Paris (1963).
7. H. Eiber, Proceedings Sixth International Conference on Ionization Phenomena in Gases, Societe d'Edition et de Recherche Publicitaire Imprimeurs, Paris (1963).
8. M. Saporoschenko, Private Communication; also J. Chem. Phys. 42, 2760, (1965) and two articles to be published in The Physical Review (both are scheduled for Vol. 139, No. 2A, July 19, 1965).
9. Technical Report No. 1, Project No. A-781 (Research Contract No. AF 49(638)-1392), Georgia Institute of Technology, Atlanta, Georgia (28 February, 1965).
10. D. W. Martin, W. S. Barnes, G. E. Keller, D. S. Harmer, and E. W. McDaniel, Proceedings Sixth International Conference on Ionization Phenomena In Gases, Vol. I, pp. 295-296, Societe d'Edition et de Recherche Publicitaire Imprimeurs, Paris (1963).
11. J. A. Dahlquist, J. Chem. Phys. 39, 1203 (1963).
12. R. N. Varney, Phys. Rev., 89, 708 (1953).
13. G. E. Keller, D. W. Martin, and E. W. McDaniel, accepted by The Physical Review (1965).
14. R. L. Jory, Thesis, Australian National University (1964), (unpublished).

LIBRARY DOES NOT HAVE *SEMIANNUAL TECHNICAL STATUS REPORT #1*

SEMI-ANNUAL TECHNICAL STATUS REPORT NO. 2

PROJECT A-781

MASS SPECTROMETRIC STUDY OF LOW FIELD MOBILITY,  
DIFFUSION, AND REACTIONS OF IONS IN GASES

D. W. MARTIN  
D. L. ALBRITTON  
T. M. MILLER  
E. W. McDANIEL

NOTICE

This document is not to be used by anyone.

Prior to 9-1 1967  
without permission of the Research Sponsor  
and the Experiment Station Security Office.

Research Contract No. AF 49(638)-1392

1 April 1965 to 30 September 1965  
Issued September 1965

Prepared for  
Air Force Office of Scientific Research  
Office of Aerospace Research  
Washington 25, D. C.

September

1965



Engineering Experiment Station  
GEORGIA INSTITUTE OF TECHNOLOGY  
Atlanta, Georgia

GEORGIA INSTITUTE OF TECHNOLOGY  
Engineering Experiment Station  
Atlanta, Georgia

SEMI-ANNUAL TECHNICAL STATUS REPORT

PROJECT A-781

MASS SPECTROMETRIC STUDY OF LOW FIELD MOBILITY,  
DIFFUSION, AND REACTIONS OF IONS IN GASES

By

D. W. MARTIN  
D. L. ALBRITTON  
T. M. MILLER  
E. W. McDANIEL

RESEARCH CONTRACT NO. AF 49(638)-1392

1 APRIL 1965 to 30 SEPTEMBER 1965  
Issued September, 1965

Performed for  
AIR FORCE OFFICE OF SCIENTIFIC RESEARCH  
OFFICE OF AEROSPACE RESEARCH  
WASHINGTON 25, D. C.

## TABLE OF CONTENTS

	Page
I. INTRODUCTION. . . . .	1
II. OBJECTIVES AND SCOPE OF THE RESEARCH. . . . .	1
III. EXPERIMENTAL APPARATUS AND METHOD . . . . .	3
IV. TRAVEL AND PUBLICATIONS DURING THE REPORT PERIOD. . . . .	5
V. REFERENCES CITED. . . . .	9

## LIST OF FIGURES

1. Side View of the Major Components of the New Ultra-High-Vacuum Drift Tube Mass Spectrometer Apparatus . . . . .	6
2. Detail View of the Essential Elements of the Ion Source, Drift Field Electrode System, Ion Sampling System, and the Mass Measurement and Detection Systems	7

## I. INTRODUCTION

The research that has been performed under Research Contract No. AF 49 (638)-1392 is a segment of a program that has been in progress at the Georgia Institute of Technology for several years. This work has been partially supported from its inception by the Air Force Office of Scientific Research under earlier contracts and grants. All phases of the research conducted up to the beginning of 1965 have been summarized in the literature.<sup>1-14</sup> This report describes a new, improved version now under construction of the apparatus which has been in service here for the last several years. The new apparatus is expected to go into operation before the end of 1965.

## II. OBJECTIVES AND SCOPE OF THE RESEARCH

The continuing broad objective of this research program has been the development and exploitation of a method of performing mass-spectrometric analyses of ion populations which have drifted for appreciable and controllable distances and times through a gas under low field conditions. Such a method permits direct positive identification of the ion species that are present under given conditions, such as those of a mobility measurement. It is further possible to make separate measurements of the mobilities and in principle also the diffusion coefficients of each species present in systems where more than one type of ion may occur. Finally, by means of controlled variations of the drift conditions, it is possible to observe and study ion-molecule reactions that may be occurring in the gas.

Definite identification of the ion species under observation has long remained one of the most vexing problems in many areas of gaseous electronics, most notably in situations such as mobility measurement where the ions remain



in the gas for appreciable times and suffer many low energy collisions. Even if the initial ion production pattern of the source in use is well understood from conventional mass spectrometer studies, the ion population may subsequently be altered radically by ion-molecule reactions of any of several general types. These include (1) transfer of the ionic charge to another species of molecule of lower ionization potential, often an impurity, and (2) the formation by essentially chemical reactions of secondary ions, often of molecular types that do not even exist as neutral molecules. Another possibility that has often been discussed<sup>15</sup> is (3) the formation of more or less stable "clusters" by the polarization attachment of one or more neutral molecules to the ion. The reaction cross sections for any of these processes may be very large, so that they may be of importance even if one of the reactants is an impurity of very low relative concentration.

Much of the existing information about ion-molecule reactions has been obtained with "high pressure" mass spectrometers, in which the gas pressure in the source region may be made great enough that some of the newly formed ions may suffer one or more collisions before passing out of the exit slit into the high vacuum of the spectrometer proper.<sup>16</sup> The mean collision energies are generally well above thermal values, and the number of collisions per ion is small, so that it has not generally been possible to approach the equilibrium low field ion spectrum with such instruments. Several other experiments had been reported<sup>17</sup> several years ago that involved the mass-analysis of an ion population present in a truly high pressure region, but none of these had been designed with quite the same objectives and given quite the same combination of features as the apparatus that has been

developed in this program.

Relatively recently, groups at several other laboratories have constructed apparatus that is similar at least in general concept to that evolved in the present program, and have undertaken studies having very similar objectives. Results that have been reported<sup>18-20</sup> have been for the most part in quite good agreement with results which we have obtained.<sup>5,12,13</sup>

### III. EXPERIMENTAL APPARATUS AND METHOD

The apparatus developed in this program for the study of drift velocities, diffusion coefficients, and ion-molecule reactions of mass-identified ions is called a "drift tube mass spectrometer." The version of the apparatus used for all the measurements performed to date has been exhaustively described;<sup>7,13,21</sup> hence, this section will deal only with the new apparatus now in its final stages of construction.

A description of the apparatus as it will exist in its final form follows: a 20-inch long, 12-inch diameter drift tube contains the gas under study at a pressure of up to about 2 torr, and ions are produced inside this tube by an ion source which utilizes a beam of magnetically confined electrons. These ions diffuse down the drift tube under the influence of an axial electric field, whose strength determines the average steady-state ionic energy for a given gas pressure. (The ratio of the electric field  $E$  to the gas pressure  $p$  can be made sufficiently low that ions can be studied at energies down to thermal. At higher  $E/p$  values, the average ionic energy in this apparatus may be made to be as high as about 0.5 eV.) A sample of the ion population at the remote end of the drift tube flows through a 1/32-inch diameter exit aperture and passes through a slit system into a field-

free differential pumping section. The ions then enter a separately pumped mass spectrometer where they are analyzed and then detected by an ion multiplier tube operated as a pulse counter. The number of collisions that an ion undergoes with molecules during its travel down the drift tube may be varied over a wide range by changing the gas pressure and/or the position of the source, which can be moved continuously over a distance of 17 inches down the axis from the outside without the drift tube having to be opened. Information concerning the nature and rate of ion-molecule reactions which occur is revealed by the resulting changes in the ionic mass spectrum. The ion source may either be operated continuously or pulsed periodically. In the latter case, the pulses produced by ions of any particular charge-to-mass ratio can be sorted electronically according to their time of arrival in the mass spectrometer, so that the distribution of drift times for the particular species is obtained. The locations and shapes of the peaks in the drift time spectrum yield information on the drift velocities, diffusion coefficients, and reaction rates of the ions. The apparatus can be used for studies of both positive and negative ions. The facility described here is unique. It will permit direct studies of ion-molecule reactions under experimental conditions hitherto unobtainable and also allow the accurate measurement of transport properties of ions whose identities are simultaneously and unambiguously identified in a mass spectrometer.

A detailed discussion of the considerations underlying the design of the new apparatus appeared in a recent annual report<sup>22</sup> and will not be repeated here. The design of the new equipment was also described in Quebec in August, 1965 at the Fourth International Conference on the Physics of

Electronic and Atomic Collisions. The main features of construction are shown here in Figures 1 and 2. The large, ultra-high-vacuum tank shown in the center of Figure 1 houses the drift tube, movable ion source, differential pumping barrier, and rf quadrupole mass spectrometer. An isometric view of the interior of the drift tube proper appears in Figure 2. Construction or procurement of all of the components shown in these two figures has been completed at the time of this writing, and final assembly has begun. It is expected that the entire apparatus, including ancillary pumping and electronic equipment not visible in the drawings, will be in operation by the end of 1965.

#### IV. TRAVEL AND PUBLICATIONS DURING THE REPORT PERIOD

D. W. Martin and E. W. McDaniel attended the Fourth International Conference on the Physics of Electronic and Atomic Collisions in Quebec, August 2-6, 1965. At this conference, E. W. McDaniel served as a session chairman and was appointed to the International Advisory Committee on Atomic Collisions. This committee is charged with the responsibility of making recommendations concerning definitions and nomenclature and of planning future conferences. A paper<sup>12</sup> dealing with the Georgia Tech measurements on nitrogen and hydrogen ions and with the design of the new drift tube mass spectrometer was read by D. W. Martin.

E. W. McDaniel gave seminar talks at the University of Florida and the National Bureau of Standards (Boulder, Colorado) and conferred with the atomic collisions research groups at these institutions.

E. W. McDaniel attended a meeting of the Executive Committee of the Gaseous Electronics Conference in Minneapolis. The Georgia Institute of

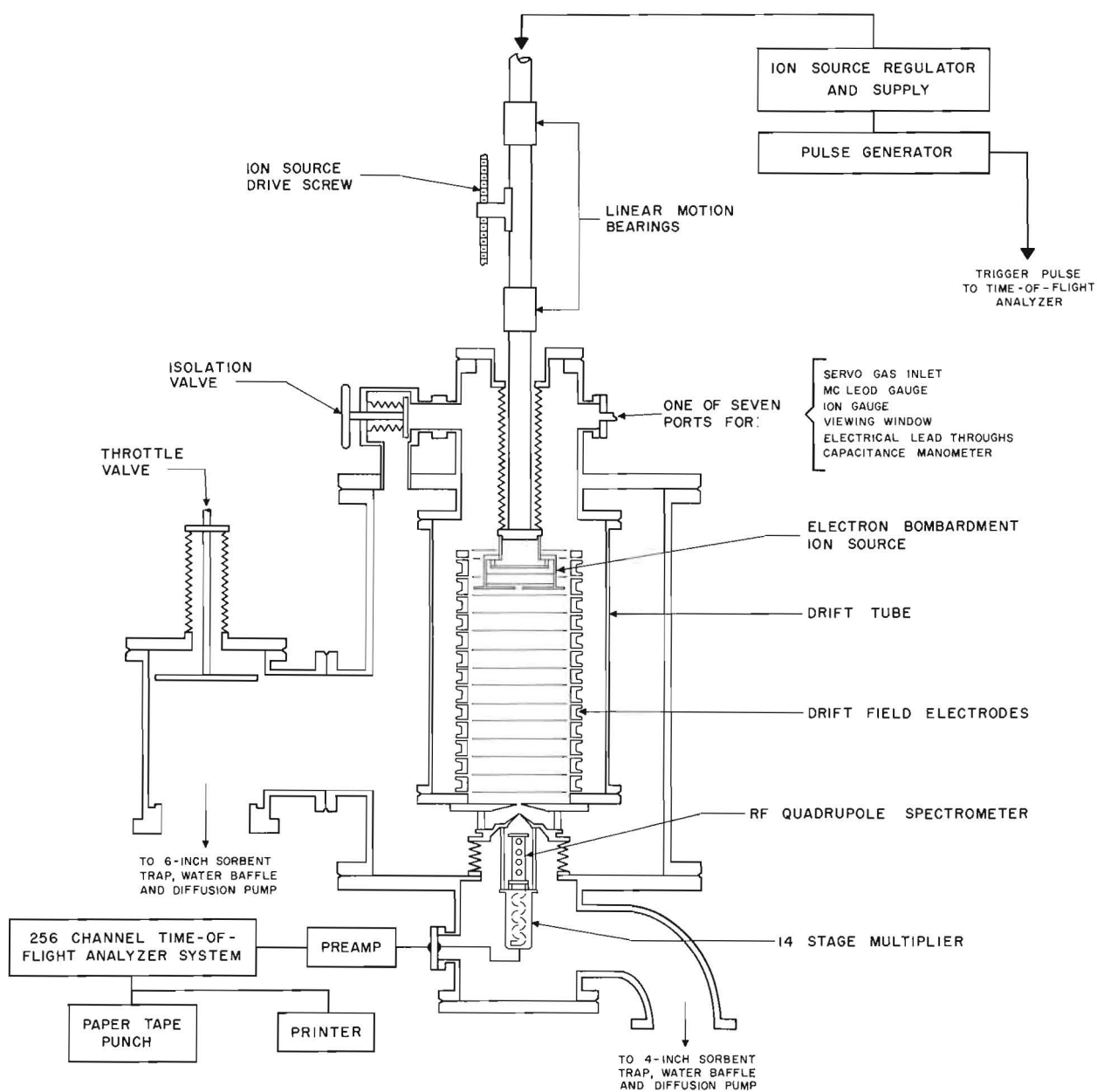


Figure 1. Side View of the Major Components of the New Ultra-High-Vacuum Drift Tube Mass Spectrometer Apparatus

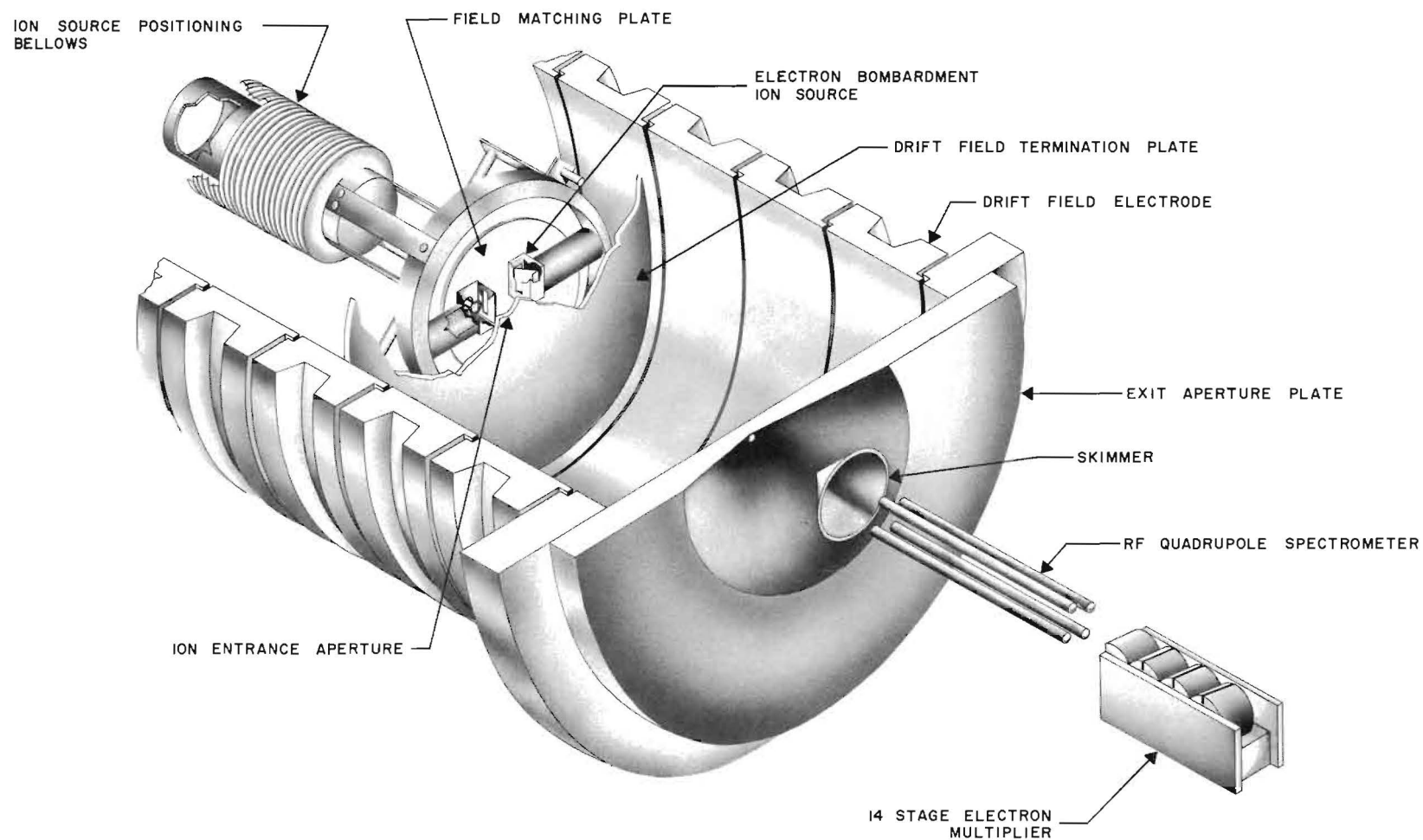


Figure 2. Detail View of the Essential Elements of the Ion Source, Drift Field Electrode System, Ion Sampling System, and the Mass Measurement and Detection Systems

Technology has been selected as the site of the 1966 Gaseous Electronics Conference.

Respectfully submitted.

David W. Martin  
Project Director

## V. REFERENCES CITED

1. E. W. McDaniel and H. R. Crane, "Measurements of the Mobilities of the Negative Ions in Oxygen and in Mixtures of Oxygen with the Noble Gases, Hydrogen, Nitrogen, and Carbon Dioxide," *Rev. Sci. Inst.* 28, 684 (1957).
2. E. W. McDaniel and M. R. C. McDowell, "Low-Field Mobilities of the Negative Ions in Oxygen, Sulfur Hexafluoride, Sulfur Dioxide, and Hydrogen Chloride," *Phys. Rev.* 114, 1028 (1959).
3. E. W. McDaniel and D. W. Martin, "Source of Thermal Ions for Use in Gases at High Pressures," *Rev. Sci. Inst.* 31, 660 (1960).
4. E. W. McDaniel, "Langevin's Theory of the Mobility of Gaseous Ions," AFOSR Document TN-60-865 (1960).
5. W. S. Barnes, D. W. Martin, and E. W. McDaniel, "Mass Spectrographic Identification of the Ion Observed in Hydrogen Mobility Experiments," *Phys. Rev. Letters* 6, 110 (1961).
6. D. W. Martin, E. W. McDaniel, and M. L. Meeks, "On the Possible Occurrence of  $H_3^+$  in Interstellar Space," *Astrophysical Journal* 134, 1012 (1961).
7. E. W. McDaniel, D. W. Martin, and W. S. Barnes, "Drift Tube-Mass Spectrometer for Studies of Low-Energy Ion-Molecule Reactions," *Rev. Sci. Inst.* 33, 2 (1962).
8. E. W. McDaniel, et al., "The Role of Atomic Collisions in Space Phenomena," invited paper presented at International Symposium on Space Phenomena and Measurement, Detroit, Michigan (October, 1962), published in *IEEE Transactions on Nuclear Science*, Vol. NS-10, No. 1, 111-118 (1963).
9. D. W. Martin, W. S. Barnes, G. E. Keller, D. S. Harmer, and E. W. McDaniel, "Mobilities of Mass-identified Ions in Nitrogen," presented at Sixth Int. Conf. on Ionization Phenomena in Gases, Paris (July, 1963), proceedings published by S.E.R.M.A., Paris, (1964), Vol. I, p. 295.
10. E. W. McDaniel, "Ion-Molecule Reactions and Ion Mobilities," invited paper presented at Meeting of S.E. Section of American Physical Society, Chattanooga, Tennessee, November, 1964.
11. E. W. McDaniel, "The Study of Ionic Collisions by Swarm Methods," invited paper presented at Gordon Conference on Molecular Beam Methods and Collision Processes, New Hampton, New Hampshire, 1965.
12. E. W. McDaniel, G. E. Keller, D. L. Albritton, T. M. Miller, and D. W. Martin, "Studies of Ionic Drift Velocities and Ion-Molecule Reactions



- in a Drift Tube Mass Spectrometer," Fourth International Conference on the Physics of Electronic and Atomic Collisions, Quebec, 1965.
13. G. E. Keller, D. W. Martin, and E. W. McDaniel, "General Considerations Concerning Apparent Mobilities in Mixed Ion Populations; Drift Velocities of Mass-Identified  $N^+$ ,  $N_2^+$ ,  $N_3^+$  and  $N_4^+$  Ions in Nitrogen," Physical Review (in press).
  14. E. W. McDaniel, "Slow Ion-neutral Collisions," a review to appear in "Methods of Experimental Physics," Volume on Atomic Physics edited by B. Bederson and W. L. Fite, Academic Press, New York.
  15. E. W. McDaniel, Collision Phenomena in Ionized Gases, Wiley, New York, 1964, pp. 448-451.
  16. For a general discussion and extensive references, see E. W. McDaniel, op. cit., p. 452.
  17. E. W. McDaniel, loc. cit.
  18. K. B. McAfee and D. Edelson, Proceedings Sixth International Conference on Ionization Phenomena in Gases, Societe d'Edition et de Recherche Publicataire Imprimeurs, Paris (1963).
  19. H. Eiber, Proceedings Sixth International Conference on Ionization Phenomena in Gases, Societe d'Edition et de Recherche Publicataire Imprimeurs, Paris (1963).
  20. M. Saporoschenko, J. Chem. Phys. 42, 2760 (1965); Physical Review 139, A349, A352 (1965).
  21. G. E. Keller, D. W. Martin, and E. W. McDaniel, Technical Report No. 1, Project No. A-781 (Research Contract No. AF 49(638)-1392), Georgia Institute of Technology, Atlanta, Georgia (28 February 1965).
  22. D. W. Martin, G. E. Keller, D. L. Albritton, T. M. Miller, and E. W. McDaniel, Annual Technical Status Report No. 1, Project No. A-781 (Research Contract No. AF 49(638)-1392), Georgia Institute of Technology, Atlanta, Georgia, June, 1965.

GEORGIA INSTITUTE OF TECHNOLOGY  
Engineering Experiment Station  
Atlanta, Georgia

FINAL REPORT

PROJECT A-781

MASS SPECTROMETRIC STUDY OF LOW FIELD MOBILITY,  
DIFFUSION, AND REACTIONS OF IONS IN GASES

By

D. W. MARTIN  
E. W. MCDANIEL  
D. L. ALBRITTON  
T. M. MILLER  
J. T. MOSELEY

RESEARCH CONTRACT NO. AF 49(638)-1392  
PROJECT-TASK NO. 9767-02

1 APRIL 1964 to 31 MARCH 1966  
Issued September, 1966

Research sponsored by the  
AIR FORCE OFFICE OF SCIENTIFIC RESEARCH  
OFFICE OF AEROSPACE RESEARCH  
UNITED STATES AIR FORCE

Each transmittal of the document outside the agencies  
of the U. S. Government must have prior approval of  
the AFOSR (SRGL).

## TABLE OF CONTENTS

	Page
ABSTRACT. . . . .	iii
I. INTRODUCTION. . . . .	1
II. EXPERIMENTAL CONCEPT. . . . .	3
III. EXPERIMENTAL STUDIES WITH THE OLD APPARATUS . . . . .	5
IV. CONSTRUCTION OF THE NEW DRIFT TUBE MASS SPECTROMETER. . . . .	9
V. PUBLICATIONS. . . . .	11
VI. PROFESSIONAL PERSONNEL. . . . .	11
VII. PATENTABLE INVENTIONS . . . . .	12
REFERENCES CITED. . . . .	12

DD FORM 1473

This report contains 12 pages.

## ABSTRACT

The addition, to a drift tube used for studies of the transport properties of low energy ion swarms, of mass spectrometric identification of the molecular composition of the swarm ions, has been shown to be both feasible and useful. Studies with an early version of a drift tube mass spectrometer apparatus have shown that complex mixed populations of several ion species occur, under a broad range of conditions, in swarms in both hydrogen and nitrogen gases. It appears likely that complex populations, interacting through a number of ion-molecule reactions, are more the rule than the exception, in which case mass identification is in general essential to the correct interpretation of swarm experiments. References are given to publications of the detailed results obtained for the nitrogen system, for which mean apparent drift velocities were obtained for  $N_1^+$ ,  $N_2^+$ ,  $N_3^+$ , and  $N_4^+$  ions over the range in the parameter  $E/p_0$  from 7 to 70 Volts/cm-Torr. Early results obtained for  $H_1^+$  and  $H_3^+$  ions in hydrogen gas have not been published because of inadequate control of interference from impurities in the old apparatus. The construction of a new ultra high vacuum version of the apparatus has been completed, and early test and performance data are briefly summarized.

## I. INTRODUCTION

The research performed under this contract represents a segment of a program that has been in progress at the Georgia Institute of Technology for several years. This effort has been partially supported from its inception by the U. S. Air Force Office of Scientific Research, under a succession of earlier contracts and grants. The present report is in a sense an Interim Final Report because the program is continuing beyond the term of this contract, with continuing AFOSR support through Grant No. AF-AFOSR-1118-66.

The continuing objective of this entire program has been the development of an experimental method of studying the transport properties of single, explicitly identified ion species in low energy ion swarms, including study of reactions between the ions and the molecules of the ambient gas. In many of the traditional ion swarm methods, the molecular nature of the ions observed can be inferred only indirectly, and it is usually not possible to be certain that one is not dealing with a mixture of two or more different species. It has become increasingly clear in recent years, in part from some of the results of the Georgia Tech program, that the simultaneous existence of several ion species in the swarm is of rather common occurrence, and may even be more the rule than the exception. This is in part because ions can often react with the molecules of the ambient gas to form rather unexpected new molecular ion species, whose corresponding neutral forms may not be bound and are thus unknown as stable compounds. Without a definite identification of the nature of the ions observed in a swarm experiment, the fundamental significance of the results, and of comparisons with the results of microscopic collision theory, are dubious at best.

Experimental data that can be compared meaningfully with theory are of

basic importance because of the details they may yield of the interaction forces between ions and molecules. Ion transport and reaction data are also of direct value to the understanding of discharge phenomena in gas-filled tubes and other electrical devices, in plasma physics, and in elucidating the complex processes of the upper atmosphere.

The aim of the present research program has been simply to conduct ion swarm studies that include mass spectrometric identification of the ions observed. This either permits one to determine with certainty what single species is present under given conditions, or else it permits one to make separate observations of the transport properties of each species when more than one is present.

Major experimental problems have centered about the necessity, in our method, of extracting a sample of the ion population in the relatively high pressure swarm region into the relatively high vacuum region of the mass analyzer, with due care taken not to distort the ion spectrum in the process. The "drift tube mass spectrometer" apparatus that has been developed for these studies was unlike any other in existence at the time this program first began; however, the simultaneous development of apparatus designed for much the same purposes is now known to be in progress at several other laboratories. The early results that have been obtained elsewhere<sup>1,2</sup> in the last two or three years have been in rather good agreement with the similar results of the Georgia Tech program, for the most part. We venture to suggest that as the techniques improve, we will see a large part of all the swarm studies of the past redone with the inclusion of mass analysis.

During the two year term of this contract (1 April, 1964 to 31 March, 1966), the Georgia Tech program has consisted of two distinct phases, which

will be treated separately in this report. The first phase involved our original drift tube mass spectrometer apparatus, which had been developed to a fully operational stage in an earlier period. Experimental studies with this apparatus, already in progress, continued into the present period, and were concluded about midway in the period. This phase will be treated in Section III. Concurrent with this effort, we began early in the period the construction of a completely new and much improved apparatus, in the design of which the most modern techniques of ultra-high vacuum were applied throughout. This effort was brought to a fully successful conclusion just before the close of the period and will be treated in Section IV.

## II. EXPERIMENTAL CONCEPT

Both the original apparatus and the recently completed new apparatus represent the same general concept. A large, cylindrical drift tube contains a localized ion source, positioned on the axis of the tube, and a set of annular electrodes to establish a uniform, weak, axial electric field. The source may be pulsed to produce a short burst of ions, which then drift down the axis under the influence of the applied field, diffusing in and perhaps also reacting with the molecules of the gas filling the tube. A sampling aperture in the center of the end plate communicates, through two stages of differential pumping, with an evacuated region containing a mass analyzer. The output of the detector of the mass analyzer is time-analyzed with respect to the time of the source burst. Thus the data obtained take the form of spectra of the arrival times at the detector of ions of known mass-to-charge ratio. By fitting these spectra to transport calculations of the time dependence of the ion density at the sampling aperture, which contain as parameters the mobility, dif-

fusion coefficient, and reaction rate coefficients for the particular ion-gas combination, experimental values of these coefficients can be obtained.

Apparatus which represents essentially this same general concept has been under development recently in several laboratories,<sup>1,2</sup> as has been mentioned previously. Our apparatus has a number of special features, however, not all of which are shared by any one of the others, which we believe make it unique:

1. The differential pumping capabilities permit a gas pressure in the drift tube that is high enough (1 Torr), and the net drift distance in the gas may be made great enough (up to 17 in), that the mean residence times of the ions in the gas may be made very long compared to the mean collision time or the duration of the source burst. The mean number of low energy collisions per ion may readily be made greater than  $10^5$ .

2. The ion source utilizes bombardment of the gas, in a nearly field-free region, by a magnetically confined beam of electrons, so that the initial spatial extent of the ion burst is limited and well defined. Further, the maximum electron energy is relatively well defined and is variable, so that one may selectively form only primary ion species of low appearance potentials, if desired.

3. The source is physically movable along the drift tube axis, permitting variation of the net drift distance, and hence of the mean drift time, with all other parameters held constant. This feature will be of great value in establishing the uniqueness of the set of empirical values of the transport coefficients that produce the best fit between the data and the transport calculation. This feature also permits the cancellation of end effects through the use of difference techniques.

4. The sampling aperture is an effusion type orifice, and the differen-



tially pumped region between it and the high vacuum analyzer region has been made completely field-free, as far as possible, so that the mass spectra obtained will be truly representative of the ion population in the drift tube gas. It is sought to avoid both primary mass discrimination effects in the orifice, and distortions of the mass spectra due to collisions, after leaving the drift tube, at higher mean energies than prevailed during the drift phase.

5. The transmission efficiency of the sampling system is consequently very small, so that single-particle detection and the use of low noise counting techniques is mandatory. It must be possible to take data under conditions in which less than one ion is detected per source burst, and the time analysis scheme used involves electronic sorting of the detector pulses into discrete time channels. (Data have been taken successfully with total count rates as low as 10 ions per minute, requiring accumulation times for a single arrival-time spectrum of several hours. Obviously, great stability is required of all experimental parameters, including in particular the gas pressure in the drift tube.)

As mentioned above, this general description applies equally to both the old apparatus and the new. Some of the more relevant differences between them will be mentioned in the following sections.

### III. EXPERIMENTAL STUDIES WITH THE OLD APPARATUS

Our original drift tube mass spectrometer apparatus was already in existence at the beginning of the term of this contract. In general concept, it conformed in all respects to the description given in Section II. The mass analyzer was of the  $60^\circ$  magnetic-deflection type, with a six-inch radius. After traversing the field-free differential pumping region, the low energy ions passed through the spectrometer entrance slit into a region of high vacuum,

where they were accelerated to energies varying from 1.0 to 2.5 keV for analysis. After analysis, the ions were further accelerated to 4.0 keV energy for detection. The detector was a nude 10-stage electron multiplier. It was estimated that the multiplier and its associated circuitry detected the incident single ions with an efficiency of about 50%, while the number of spurious "noise" pulses recorded was of the order of less than 10 per minute. The time sorting operation was performed by a 20-channel time analyzer having channel widths of 10, 30, 100, or 400 microseconds. The time width of the ion source burst was usually set at 20 microseconds.

An extended study of the system of nitrogen atomic and molecular ions in nitrogen gas was in progress at the beginning of this contract period and was continued into this period. By about the middle of the period, it was felt that this study had been carried to the limit of the capabilities of the existing apparatus, so it was concluded at that point. All of the results obtained have been described in detail in a lengthy technical report,<sup>3</sup> which includes a detailed description of the apparatus. The results were also published in an article, in which a discussion is given of the impact of this type of data on the field of ion transport studies.<sup>4</sup> In view of this coverage of the results, they will not be repeated here. Data of sufficient quality to permit the evaluation of what we have called the mean apparent drift velocity were obtained for all four of the species  $N_1^+$ ,  $N_2^+$ ,  $N_3^+$ , and  $N_4^+$  over the range of the parameter  $E/p_0$  from 7 to 70 Volts/(cm-Torr). The range of gas pressures utilized was from 0.05 to 0.30 Torr, for the most part.

The reproducibility and self consistency of the mean apparent drift velocity determinations for the nitrogen ions was excellent, and it is felt that the reported values of this quantity have absolute accuracies of the order of

5%, and even better relative accuracies among the several species. However, with regard to the details of the drift-time spectra obtained, the distributions were in general much broader than would be expected from the transport calculations. The implied values of the diffusion coefficients were thus much too large, and in view of this general disagreement with theory, no attempts were made to evaluate reaction rate coefficients from the data. (However, it could be ascertained with confidence from the general form of the data that the old suggestion, that  $N_2^+$  and  $N_4^+$  ions interconvert into each other in collisions with gas molecules,<sup>5</sup> is basically correct.)

It is evident even from this very brief description of the results obtained that the old apparatus was completely successful in demonstrating the feasibility of sampling low energy ions from a swarm environment into a high vacuum mass analyzer, and further, it demonstrated admirably that there were interesting and provocative new results to be obtained in this way. However, the difficulties mentioned concerning the excessive width of the arrival-time distributions were indicative of the fact that this apparatus was inadequate to perform good measurements of any transport properties of the swarm other than the mean drift velocity. It has long been well known that reproducible and significant transport measurements are possible only with careful attention to extremely high purity of the sample gas (and hence to extreme cleanliness of the drift tube), and to geometrical precision in the construction of the drift tube. Both of these requirements had been compromised to a considerable degree in this first developmental version of the experiment. There had been first of all the need for flexibility and ready access to the drift tube, so that modifications could readily be made as the need arose. Other compromises had been made in the interest of keeping costs within reason, in

view of the speculative nature, in the beginning, of the whole concept. Neoprene "O" rings had been used for vacuum seals in many places, and many of the flanges were not properly designed to permit ready conversion to all-metal seals. This drift tube could, of course, not be baked. The vital need to make the ion source movable had become evident only well along in the development, and the arrangement to provide this feature had been improvised to require as little modification of the then existing apparatus as possible. It did not provide high precision in the location of the source, and it placed a good bit of mechanical gadgetry inside the drift tube, where it was in contact with the sample gas and added to the contamination problems. Although a number of measures were taken that substantially improved upon the contamination situation, this problem continued to be one of the principal limitations of the apparatus.

Once our experience with this apparatus had demonstrated the feasibility of the method and established firmly what kind of experimental arrangements were workable, the decision was made to build a completely new apparatus. In its design, most of the undesirable features of the old apparatus were avoided, and full advantage was taken of the considerable advances of recent years in the technology of "ultra-high" vacuum. Construction of this new apparatus was begun early in this contract period and will be dealt with in Section IV.

As indicated above, the nitrogen studies already in progress with the old apparatus were continued concurrently during about the first half of the period, and they were concluded with the mean apparent drift velocity determinations outlined above. It was believed that further effort could more profitably be concentrated on the development of the new apparatus than on attempts to make any further improvements in the performance of the old. It is planned that further studies of the nitrogen system using the new apparatus will be made in

the coming period.

In conclusion of this section, it is mentioned that a brief series of experiments on the system of hydrogen ions in hydrogen gas was also made with the old apparatus. Preliminary values of the mean drift velocities of  $H_1^+$  and  $H_3^+$  ions were obtained, which at first appeared to be in good agreement with the recent similar information from another laboratory.<sup>6</sup> It was then noted, however, that a contaminant ion of mass 29 (presumably  $N_2H^+$ ) was present with a large abundance and appeared to have the same mean apparent drift velocity as did  $H_3^+$ . This fact made all of the results highly suspect, so this study was also terminated, to be resumed again later with the new apparatus.

By the close of this report period, the old apparatus had been taken out of service and dismantled.

#### IV. CONSTRUCTION OF THE NEW DRIFT TUBE MASS SPECTROMETER APPARATUS

The concept of the new apparatus also conforms in all respects to the general description given in Section II. In contrast to the old apparatus, the mass analyzer that has been installed initially is a small rf quadrupole instrument,<sup>7</sup> and an improved 14-stage electron multiplier of greater sensitivity has been used as the detector. Larger and faster vacuum pumps have been used, and the conductance geometry for differential pumping at the drift tube exit aperture has been very substantially improved. The old 20-channel time analyzer, with its minimum channel width of 10 microseconds, has been replaced by a vastly superior 256-channel analyzer having channel widths as small as 0.25 microsecond.

In most other respects, the differences between the new and the old apparatus are largely a matter of the mechanical details of construction. The principal design criteria were detailed and their motivation explained in a previous

report.<sup>8</sup> Metal gaskets have been used throughout, the system is fully bakable, and it is equipped with heating mantles for this purpose.

The base vacuum of the drift tube is lower than  $1 \times 10^{-9}$  Torr. A typical background pressure before filling with the test gas (i.e., with the pumping port closed and the source filament on) is  $5 \times 10^{-7}$  Torr. (At the lower test pressures, say  $2.5 \times 10^{-2}$  Torr, this represents an upper limit to the impurity concentration, due to leaks and outgassing, of 20 parts per million.) In studies with hydrogen gas, the gas is admitted through a palladium diffusion tube that admits negligible additional impurities ( $< 1$  ppm).

The pumping system has proved adequate to handle the gas load accompanying a drift tube pressure of 1 Torr. The pressure in the differentially pumped region containing the mass spectrometer and electron multiplier does not exceed  $7 \times 10^{-6}$  Torr. Preliminary intensity measurements indicate a minimum count rate in hydrogen gas of 500 counts per minute over all of the range of the parameter  $E/p_0$ , from 0.5 to 200 Volts/cm-Torr.

The small quadrupole mass spectrometer presently installed has a maximum resolving power of about 40. Normally the analyzer is operated at much lower resolving power to gain intensity. The ability to alter the resolving power at will, by simple external settings of the control circuit, has proven to be one of the most useful features of this instrument.

The stability of the system has exceeded expectations. Short term reproducibility (over less than 1 day) in the values of the mean apparent drift velocity is better than one percent; over periods of weeks, the values have been reproduced to within two percent.

The stability data just given were included here for the sake of completeness, but actually draw on experience with the apparatus since the close of

the period covered by this report. Actually, the final assembly of the whole system was just completed and the initial tests of the total system performance were just beginning at the close of the period. In the test period, certain noise problems with the detector were encountered and have been dealt with, after which the accumulation of data on the hydrogen system was begun. Good results are being obtained, but they will not be reported here, since they lie outside the scope of this report.

## V. PUBLICATIONS

### Technical Report:

"Low-Field Drift Velocity Measurements on Mass-Identified Ions in Nitrogen," G. E. Keller, D. W. Martin, and E. W. McDaniel, Technical Report No. 1, Project A-781, Georgia Institute of Technology, Atlanta, Georgia, February 28, 1965.

### Journal Article:

"General Considerations Concerning Apparent Mobilities in Mixed Ion Populations: Drift Velocities of Mass-Identified  $N^+$ ,  $N_2^+$ ,  $N_3^+$ , and  $N_4^+$  Ions in Nitrogen," G. E. Keller, D. W. Martin, and E. W. McDaniel, The Physical Review 140, A1535 (1965).

### Oral Paper:

"Studies of Ionic Drift Velocities and Ion-Molecule Reactions in a Drift-Tube Mass Spectrometer," E. W. McDaniel, G. E. Keller, D. L. Albritton, T. M. Miller, and D. W. Martin. Presented at the IV-th International Conference on the Physics of Electronic and Atomic Collisions, held in Quebec, Canada (1965).

## VI. PROFESSIONAL PERSONNEL

Professors David W. Martin and Earl W. McDaniel participated in this research and were jointly responsible for its conduct. Dr. George E. Keller was awarded the Ph.D. in Physics in June, 1965, by the Georgia Institute of Technology; his dissertation, entitled "Low-Field Drift Velocity Measurements on Mass-Identified Ions in Nitrogen," was based on the research performed with the old apparatus.

## VII. PATENTABLE INVENTIONS

No patentable inventions have been made by any of the personnel engaged in this research.

Respectfully submitted,

David W. Martin  
Project Director

## REFERENCES CITED

1. K. B. McAfee and D. Edelson, Proceedings of the Sixth International Conference on Ionization Phenomena in Gases, Vol. I, 299 (SERMA, Paris, 1963); J. A. Morrison and D. Edelson, J. Appl. Phys. 33, 1714 (1962); D. Edelson, J. A. Morrison, and K. B. McAfee, Ibid. 35, 1682 (1964); D. Edelson and K. B. McAfee, Rev. Sci. Instr. 35, 187 (1964).
2. M. Saporoschenko, Phys. Rev. 139, A352 (1965); M. Saporoschenko, J. Chem. Phys. 42, 2760 (1965).
3. G. E. Keller, D. W. Martin, and E. W. McDaniel, Technical Report No. 1, Project A-781, Georgia Institute of Technology, Atlanta, Georgia (1965).
4. G. E. Keller, D. W. Martin, and E. W. McDaniel, Phys. Rev. 140, A1535 (1965).
5. R. N. Varney, Phys. Rev. 89, 708 (1953); F. R. Kovar, E. C. Beaty, and R. N. Varney, Phys. Rev. 107, 1490 (1963).
6. M. Saporoschenko, Phys. Rev. 139, A349 (1965).
7. W. Paul, H. P. Reinhard, and U. von Zahn, Zeitschrift fur Physik 152, 143 (1958).
8. D. W. Martin, G. E. Keller, D. L. Albritton, T. M. Miller, and E. W. McDaniel, Annual Technical Status Report No. 1, Project A-781, Georgia Institute of Technology, Atlanta, Georgia (1965).



UNCLASSIFIED

Security Classification

## DOCUMENT CONTROL DATA - R &amp; D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) Georgia Institute of Technology Engineering Experiment Station Atlanta, Georgia 30332		2a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED	
3. REPORT TITLE MASS SPECTROMETRIC STUDY OF LOW FIELD MOBILITY, DIFFUSION, AND REACTIONS OF IONS IN GASES		2b. GROUP	
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) Scientific, --- --- - ---Final			
5. AUTHOR(S) (First name, middle initial, last name) David W. Martin, Earl W. McDaniel, Daniel L. Albritton, Thomas M. Miller, and John T. Moseley			
6. REPORT DATE September, 1966	7a. TOTAL NO. OF PAGES 12	7b. NO. OF REFS 13	
8a. CONTRACT OR GRANT NO. Contract No. AF 49(638)-1392	9a. ORIGINATOR'S REPORT NUMBER(S) Project A-781		
b. PROJECT NO. 9767-02	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)		
c. 61445014	AFOSR 66-1857		
d. 681301			
10. DISTRIBUTION STATEMENT Each transmittal of the document outside the agencies of the U. S. Government must have prior approval of the AFOSR (SRGL).			
11. SUPPLEMENTARY NOTES		12. SPONSORING MILITARY ACTIVITY AFOSR (SRPP) 1400 Wilson Boulevard Arlington, Virginia 22209	
13. ABSTRACT <p>The addition, to a drift tube used for studies of the transport properties of low energy ion swarms, of mass spectrometric identification of the molecular composition of the swarm ions, has been shown to be both feasible and useful. Studies with an early version of a drift tube mass spectrometer apparatus have shown that complex mixed populations of several ion species occur, under a broad range of conditions, in swarms in both hydrogen and nitrogen gases. It appears likely that complex populations, interacting through a number of ion-molecule reactions, are more the rule than the exception, in which case mass identification is in general essential to the correct interpretation of swarm experiments. References are given to publications of the detailed results obtained for the nitrogen system, for which mean apparent drift velocities were obtained for <math>N_1^+</math>, <math>N_2^+</math>, <math>N_3^+</math>, and <math>N_4^+</math> ions over the range in the parameter <math>E/p_0</math> from 7 to 70 Volts/cm Torr. Early results obtained for <math>H_1^+</math> and <math>H_3^+</math> ions in hydrogen gas have not been published because of inadequate control of interference from impurities in the old apparatus. The construction of a new ultra-high vacuum version of the apparatus has been completed, and early test and performance data are briefly summarized.(U).</p>			